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# Peculiar Nonlinear Elasticity of Polyrotaxane Gels with Movable Cross-Links Revealed by Multiaxial Stretching

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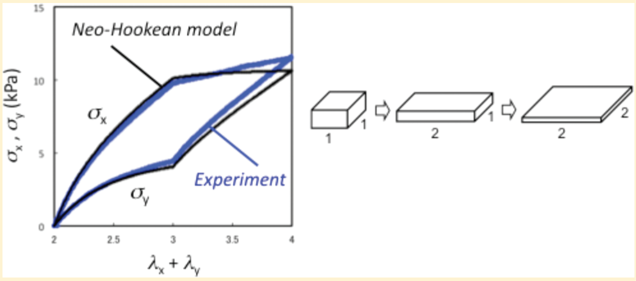
S *Supporting Information*

**ABSTRACT:** A peculiar rubber elasticity feature of polyrotaxane (PR) gels with cross-links capable of moving along network strands is revealed by general biaxial strain testing that varies the strains in the two orthogonal directions. The influence of the strain in one direction on the stress in the other direction in the PR gels with sufficiently low cross-link concentrations is much smaller than that in conventional elastomers and gels with fixed cross-links. The stress−strain behavior of the PR gels under various types of deformation is exceptionally close to the prediction of the neo-Hookean model with no explicit strain-coupling between the different principal directions other than that resulting from volume conservation. The minimal strain-coupling between different two directions is a pronounced feature for PR gels with movable cross-links to vary the network topology in response to imposed deformation.



## INTRODUCTION

Supramolecules with novel topological features have great potential for new functions and physical properties.[1−3] A typical example is given by polyrotaxanes (PRs) that have a necklace-like structure consisting of a single polymer chain with many cyclic molecules threaded onto it and two bulky moieties bound to each end.[4−6] One of the authors showed that PRs form unique soft solids (gels) when the cyclic molecules in different polymer chains are linked together.[7] In PR gels, the polymer chains are topologically interlocked by figure-of-eight cross-links (Figure 1). The network chains in PR gels are linked together entirely by topology, in contrast to those in classical gels that are tied at specific sites by covalent bonds or physical aggregations.[8] The figure-of-eight cross-links in PR gels are freely movable along the network strands and act like pulleys when the gels deform, which is called the "pulley effect".[7,9] The pulley effect is expected to have the function of varying the network configuration in response to an imposed deformation, allowing the total entropy in the deformed state to be maximized.

The unique structural features of PR gels have been revealed by small-angle neutron[10] and X-ray scattering[11] experiments. The scattering of uniaxially stretched PR gels exhibited the so-called "normal butterfly patterns" (i.e., prolate patterns normal to the stretching axis)[10] or almost isotropic pattern,[11] in contrast to the abnormal butterfly pattern (prolate pattern along the stretching axis) observed in stretched classical gels with topologically fixed cross-links. This suggests that in PR gels the frozen structural disorder is less important than the thermal fluctuation. We also observed an anomaly in the stretching-driven swelling behavior of PR gels.[12] The equilibrium Poisson's ratio, which is a measure of the induced swelling, showed a pronounced dependence on the imposed strain, whereas that of the classical gels was strain-independent. These anomalous scattering and osmomechanical properties were explained by the presence of the pulley effect that homogenized the network topology under the imposed deformation.

PR gels with movable cross-links are a new type of elastomer. The nonlinear elasticity of PR gels with movable cross-links is expected to be substantially different from that of the classical gels and elastomers.[8] In the present paper, we address this issue on the basis of the stress−strain behavior under general biaxial strain. General biaxial strain testing independently varies the strains in the two orthogonal directions ($x$- and $y$-directions) and covers a wide range of physically accessible deformations. It thus provides a definite basis for discussing all of the aspects of the nonlinear elasticity of elastomeric materials.[13,14] In this work, we have employed uniaxial stretching and the three types of biaxial deformation (Figure 2), i.e., equibiaxial stretching, pure shear deformation, and "two-step" biaxial deformation. In the equibiaxial stretching, the sample sheets were equally stretched along the two orthogonal directions ($\lambda_x = \lambda_y$), where $\lambda_i$ ($i = x, y$) is the

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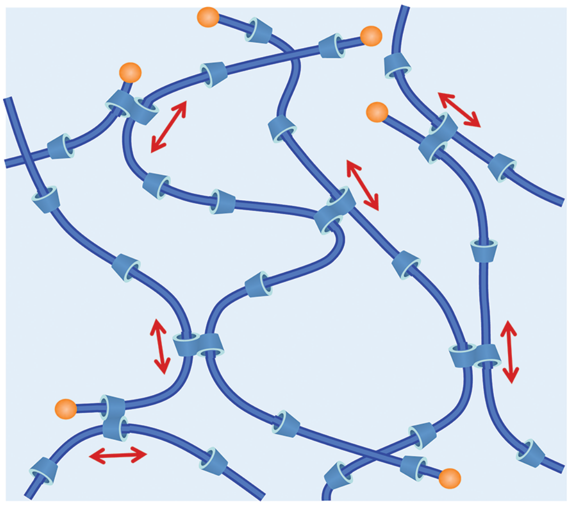

Figure 1. Schematic diagram of slide-ring gels prepared by cross-linking cyclic molecules in polyrotaxane. The slide-ring gels have figure-of-eight cross-links movable along network strands together with a finite amount of free cyclic molecules.

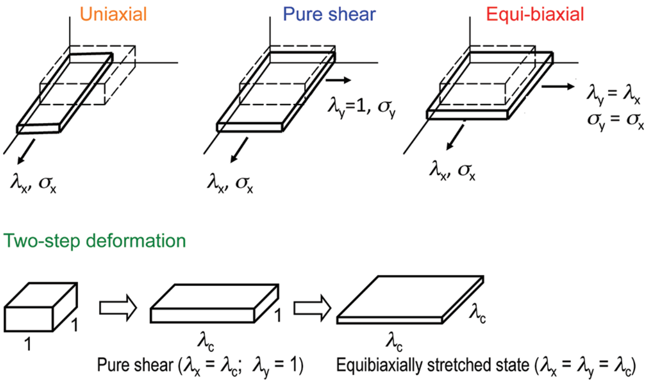

Figure 2. Four types of deformation employed in experiments.

ratio of the dimensions in the undeformed and deformed states along the $i$-axis. In the pure shear deformation, the film specimen was uniaxially stretched in the $x$-direction, while prohibiting lateral shrinking in the $y$-direction ($\lambda_y = 1$). In the two-step biaxial deformation, the gel was first deformed by pure shear up to $\lambda_x = \lambda_c$ and then stretched in the $y$-direction while maintaining $\lambda_x = \lambda_c$ until the equibiaxially stretched state of $\lambda_x = \lambda_y = \lambda_c$ was achieved. We compare the stress−strain relations under various types of deformation between the PR gels with movable cross-links and the conventional gels with fixed cross-links. We also investigate the effect of cross-link concentration on the nonlinear elasticity of the PR gels. We estimate the form of the elastic free energy of the PR gels on the basis of the stress−strain data under various modes of deformation.

## ■ EXPERIMENTAL SECTION

**Preparation of PR Gels.** The PR gels were prepared by the intermolecular cross-linking of PRs composed of $\alpha$-cyclodextrin (CD) and poly(ethylene glycol) (PEG) capped with 1-adamantanamine using 1,4-butanediol diglycidyl ether as a cross-linker.[12] The number- and weight-average molecular weights of PEG are $M_n = 1.15 \times 10^5$ and $M_w = 3.78 \times 10^5$, respectively, and the inclusion ratio (i.e., the CD filling rate to a full filling rate) for the PR was 21%. The PR contains ca. 280 CDs on a PEG chain composed of ca. 2600 ethylene glycol units. The PR was dissolved with the cross-linker in a 1.5 N NaOH aqueous solution to achieve a PR concentration of 0.15 g/mL. The cross-link concentration ($c_x$) was 5 or 10 vol %. The gelation was conducted at room temperature for 20 h in a mold. The resultant PR gel was allowed to swell fully in distilled water to wash out the unreacted materials, and thereafter the gel was gradually dried under reduced pressure. The fully dried PR network in the glassy state was swollen by adding a controlled amount of dimethyl sulfoxide (DMSO), which is a nonvolatile good solvent for the PR, to achieve a PR concentration ($c_{PR}$) of 34 wt %. The appearance of the resultant gels was transparent. This PR concentration was chosen because further swollen gels with $c_{PR} < 25$ wt % became too soft to precisely measure the tensile force using the biaxial tester, and a reduction in $c_{PR}$ to less than 40 wt % was needed to observe the pure rubber elasticity, i.e., perfect strain recovery on unloading. The PR gel with a cross-link concentration of $c_x$ and a PR concentration of $c_{PR}$ is designated as PRG-$c_x$-$c_{PR}$.

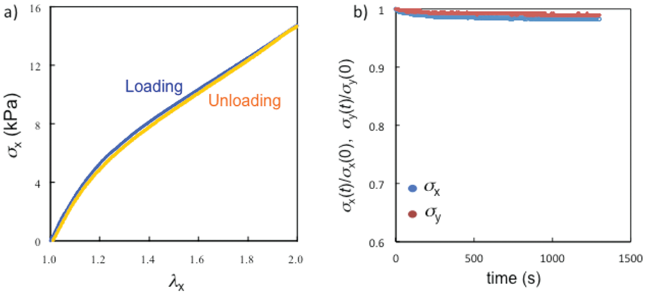

Figure 3. (a) Nominal stress−elongation curves for PRG-5-34 in the loading and unloading processes by equibiaxial stretching with a crosshead speed of 1 mm/s. No appreciable difference is observed in the loading and unloading processes. (b) Stress relaxation after the imposition of pure shear of $\lambda_x = 2$ with a crosshead speed of 1 mm/s. The time $t = 0$ corresponds to the state just after the strain imposition. The stress at each axis is reduced by the value at $t = 0$. Almost no stress relaxation (less than 3%) is observed.

**Preparation of Polyacrylamide Hydrogels.** The chemically cross-linked polyacrylamide (PAAm) gels were prepared by the radical copolymerization of an acrylamide monomer and methylenebis(acrylamide) (cross-linker) using ammonium persulfate as the initiator. The acrylamide monomer concentration was 20 wt %, and the molar ratio of [monomer/cross-linker] was 6400. Gelation was conducted at 5 °C for 24 h in a glass container. The resultant gel sheet specimen was allowed to swell in water until the swelling equilibrium was achieved. The water content in the fully swollen state is 97.0 wt %.

**Tensile Measurements.** The uniaxial and biaxial tensile measurements were conducted at room temperature using a RTM-250 (Orientec) and custom-built tester BIS-0404 (IS Giken), respectively. The typical sizes of the rectangular gel specimens used for the biaxial and uniaxial elongations were 65 × 65 × 2 mm or 50 × 10 × 2 mm, respectively. Because the gels were broken at $\lambda_x \approx 2.5$ under equibiaxial elongation in the preliminary experiments, the imposed maximum stretch was limited to 2 to allow the same specimen to be used for the measurements in different types of biaxial deformation. It was confirmed that the grid pattern drawn on the surface of a specimen was deformed in the same way as the imposed biaxial strain, excepting the region in the vicinity of the clamps. In addition, the force measured by this biaxial tester originates from the central region (50 × 50 mm) of the specimens excepting the region near the clamps (see Figure 2a in ref 15). These indicate that the biaxial strain field in the specimen is similar to the externally applied one. The specimen for uniaxial stretching was cut out from the sample sheet used for the biaxial experiments. In each deformation, the gels were stretched at a constant crosshead speed of 1 mm/s which was sufficiently slow to exclude the time effect, the details of which will be

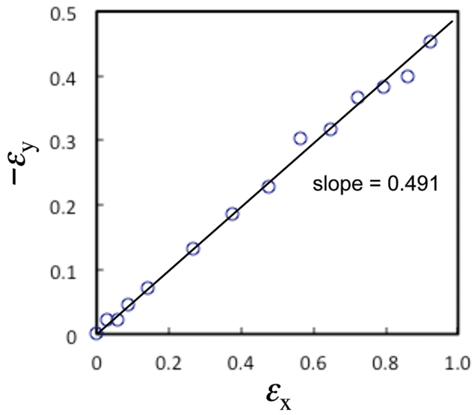

**Figure 4.** Relation of the true strains along the axes parallel and normal to the uniaxial stretching direction for PRG-5-34. The slope provides a value of Poisson's ratio.

described in the next section. The three types of biaxial deformation employed (i.e., equibiaxial stretching, pure shear, and two-step deformation) are schematically shown in Figure 2. The biaxial stretching experiments for the fully swollen PAAm hydrogel was performed in water using a custom-built tester BIS-0707 (IS Giken) equipped with a water bath.[15]

In the uniaxial stretching experiment, the deformation process was recorded with a CCD camera. The Poisson's ratio was evaluated from the dimensional changes in the directions along and normal to the stretching direction.

We confirmed the reproducibility of the data of all types of experiments using several different specimens.

## RESULTS AND DISCUSSION

Figure 3a shows the nominal stress ($\sigma_x$)−stretch ($\lambda_x$) curves in the loading and unloading processes under equibiaxial stretching at a crosshead speed of 1 mm/s for PRG-5-34. No appreciable difference in the curves for the loading and unloading processes is observed. Figure 3b shows the time dependence of stresses after the imposition of the pure shear deformation of $\lambda_x = 2$ with a crosshead speed of 1 mm/s. The stresses in the figure are reduced by those just after $\lambda_x$ reached 2. Almost no stress relaxation (less than 3%) was observed. These results in Figure 3a,b indicate that this crosshead speed is sufficiently slow to obtain the quasi-equilibrium stress−strain relations with no appreciable time effect.

Figure 4 shows the plots of the true strains ($\varepsilon$) along the axes parallel and perpendicular to the uniaxial stretching direction for PRG-5-34. The data points fall on a straight line with a slope of 0.491 in the entire range of strain examined. The slope in this plot corresponds to the Poisson's ratio ($\mu$) defined by

$$\mu = -\frac{\varepsilon_y}{\varepsilon_x} = -\frac{\ln \lambda_y}{\ln \lambda_x} \qquad (1)$$

Equation 1 is a generalized definition of $\mu$ which is applicable to finite deformation as well as small deformation. On the basis of this result ($\mu \approx 1/2$), we treat thereafter the PR gels as incompressible materials.

Figure 5 shows the stress−strain behavior for the PR gel PRG-5-34 with $c_x$ = 5 vol % (designated as PRG-$c_x$-$c_{PR}$). The nominal stress ($\sigma$)−$\lambda_x$ relation in each deformation was fairly close to the prediction of the ideal rubber elasticity (neo-Hookean) model,[13,16,17] which is the simplest model of rubber elasticity. The elastic free energy ($F$) of this model has an extremely simple

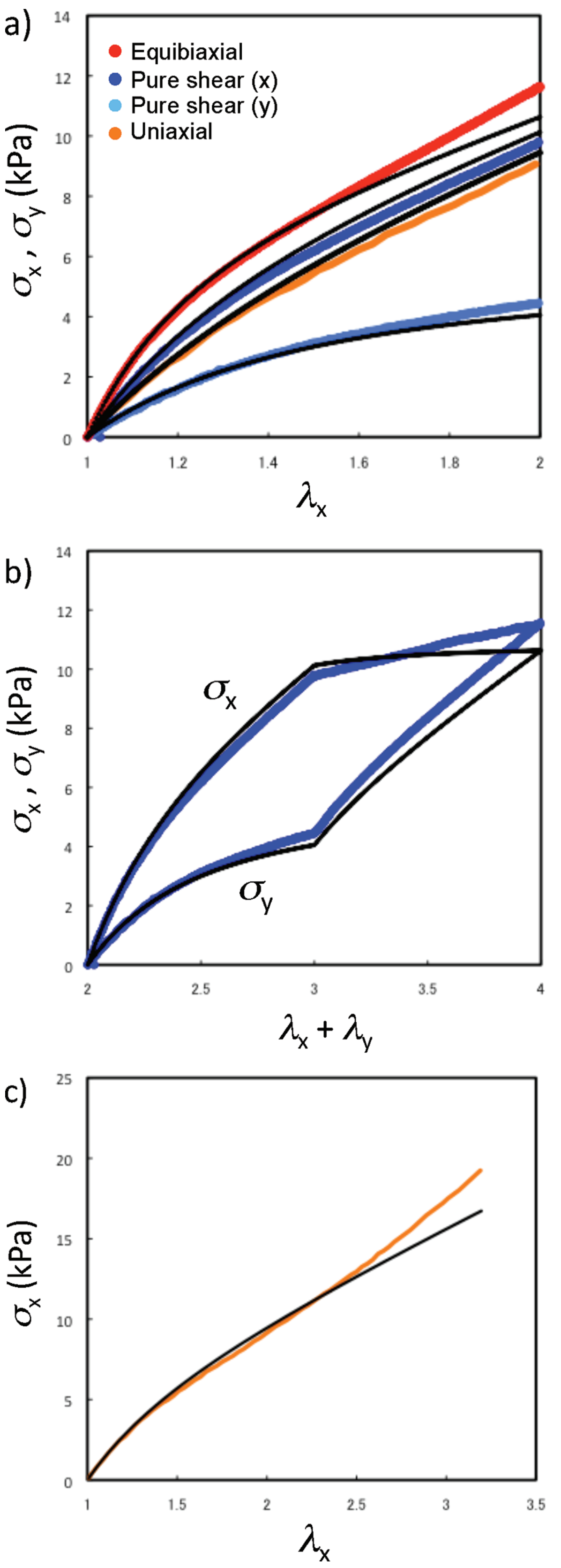

**Figure 5.** Nominal stress−elongation curves for PRG-5-34 in (a) equibiaxial stretching, pure shear, and uniaxial stretching of $\lambda \leq 2$, (b) two-step biaxial deformation, and (c) uniaxial stretching. The black lines represent the predictions of the neo-Hookean model with $G$ = 4.9 kPa.

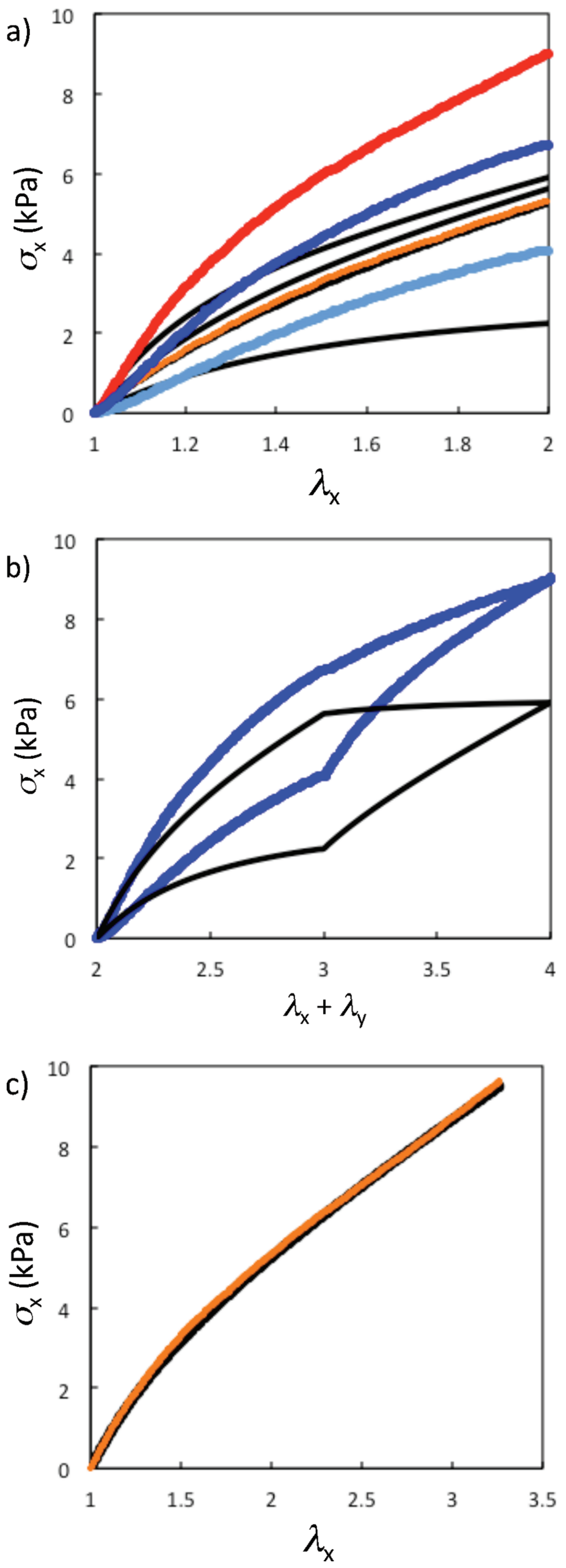

**Figure 6.** Nominal stress−elongation curves for a fully swollen polyacrylamide chemical gel in (a) equibiaxial stretching, pure shear and uniaxial stretching of $\lambda \leq 2$, (b) two-step biaxial deformation, and (c) uniaxial stretching. The black lines represent the predictions of the neo-Hookean model with $G = 3.0$ kPa. The water content in the gel is 97.0 wt %.

form containing only one material parameter, i.e., the small-strain shear modulus ($G$), involving no explicit strain-coupling term between different principal axes such as $\lambda_i\lambda_j$ ($i, j = x, y, z$ and $i \neq j$):

$$F = \frac{G}{2}(\lambda_x^{\ 2} + \lambda_y^{\ 2} + \lambda_z^{\ 2} - 3) = \frac{G}{2}(I_1 - 3) \tag{2}$$

where $I_1$ is the first invariant of deformation tensor defined by $I_1 = \lambda_x^{\ 2} + \lambda_y^{\ 2} + \lambda_z^{\ 2}$. The nominal stresses of this model in general biaxial deformation are expressed by

$$\sigma_x = G\left(\lambda_x - \frac{1}{\lambda_x^{\ 3}\lambda_y^{\ 2}}\right) \tag{3a}$$

and

$$\sigma_y = G\left(\lambda_y - \frac{1}{\lambda_x^{\ 2}\lambda_y^{\ 3}}\right) \tag{3b}$$

The corresponding expression for uniaxial deformation is given by

$$\sigma_x = G\left(\lambda_x - \frac{1}{\lambda_x^{\ 2}}\right) \tag{4}$$

A small upward deviation of ca. 10% was observed in the equibiaxial stretching of $\lambda \approx 2$ and the uniaxial stretching of $\lambda \approx 3$, but the "neo-Hookean like" behavior under various types of deformation reaching a finite stretching of $\lambda \approx 2$ was quite exceptional. It has long been known that the uniaxial data of many chemical gels and rubbers in the fully swollen state agree well with the prediction of the neo-Hookean model (eq 4).[13] However, our recent biaxial experiments using a fully swollen rubber[18] and some chemical gels with very low network concentrations (less than 5 wt %)[15] revealed that the agreement of the uniaxial data is superficial because the model obviously fails to describe the biaxial data. Figure 6 shows the corresponding example for a fully swollen polyacrylamide chemical gel with a water content of 97.0 wt %. In accordance with our previous observations for classical chemical gels,[15,18] the biaxial data markedly deviate from the predictions of the neo-Hookean model (eq 3) although the uniaxial data agree well with that.

PRG-5-34 corresponded to a slightly deswollen state ($c_{\mathrm{PR}} \approx$ 34 wt %) as compared to the state of gel preparation ($c_{\mathrm{PR}} \approx 15$ wt %). In the case of classical chemical gels, the gel prepared directly at its final concentration and that obtained via deswelling from the preparation state are different in the tensile behavior even if the concentration is identical.[19] The deswollen gels exhibit a larger deviation from the neo-Hookean model than the corresponding as-prepared gels.[19] Thus, the neo Hookean-like behavior of PRG-5-34 will not be primarily attributed to the deswelling effect, although the slide-ring gels may not be affected by the deswelling effect in the same manner as the chemical gels.

Several studies[20−25] showed that the significant degrees of intermolecular and intramolecular aggregation of CDs occurred in the PR chains in DMSO under some conditions. Recently, one of the authors[25] first determined separately the conformation of PEG in PR and the spatial distribution of CDs on PEG in DMSO by the contrast variation SANS technique: When the CD inclusion ratio (i.e., the CD filling rate to a full filling rate) for the PR is sufficiently small (27%), the CDs are not localized but are distributed randomly along the entire PEG chain. The CD inclusion ratio of the PR employed here is 21%, which is definitely smaller than the value (27%) in the SANS study. Further, the intramolecular cross-linking and aggregation between the neighboring CDs are considerably

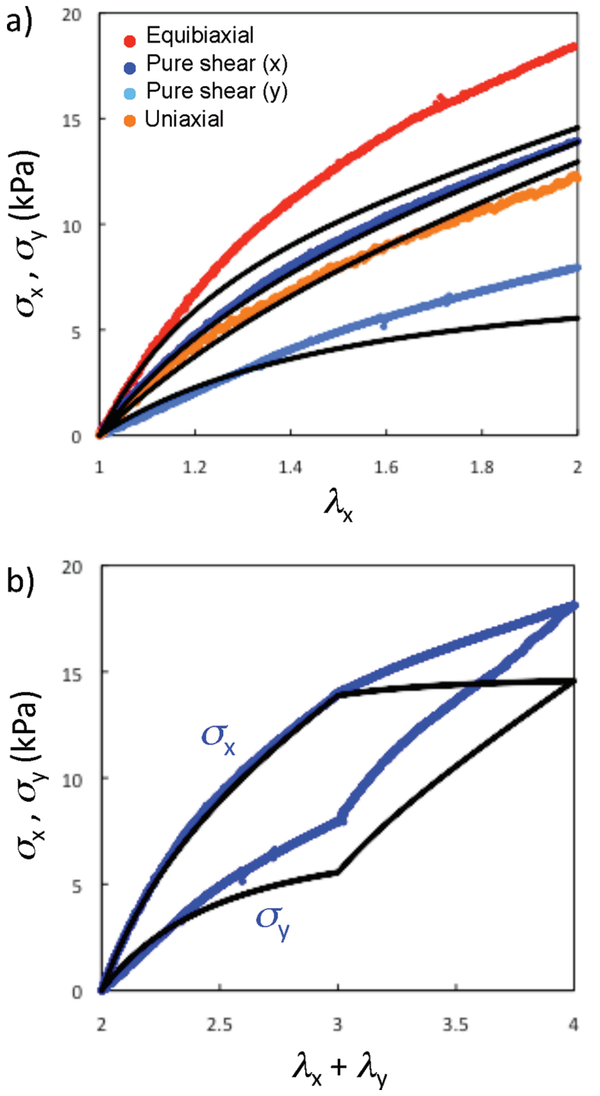

**Figure 7.** Nominal stress−elongation curves for PRG-10−34 in (a) equibiaxial stretching, pure shear, and uniaxial stretching of $\lambda \leq 2$ and (b) two-step biaxial deformation. The black lines represent the predictions of the neo-Hookean model for rubber elasticity with $G$ = 6.4 kPa.

suppressed under the cross-linking condition in the present study: The CDs are uniformly dispersed due to strong Coulomb's interaction in this concentrated NaOH aqueous solution.[20] In addition, the size of the cross-linker molecule (1,4-butanediol diglycidyl ether) is too small to link the adjacent CDs on the PR with uniformly dispersed CDs: The average distance between the neighboring CDs (on the PR with 21% of the CD inclusion ratio) corresponds to ca. 8 ethylene glycol units that is larger than the length of the cross-linker corresponding to as large as 6 ethylene glycol units. Moreover, a finite amount of hydroxyl groups on CDs is consumed by the reaction with the cross-linker, which also suppresses the aggregation of CDs. The transparent appearance of PRG-5-34 and PRG-10-34 indicates the absence of finite CD aggregations in these gels. Thus, the intermolecular and intramolecular aggregations of CDs and intramolecular cross-linking are considerably suppressed here on the basis of these molecular characteristics of PR and cross-linker and the cross-linking conditions.

An important characteristic of the neo-Hookean model is the minimal coupling between the different principal axes that

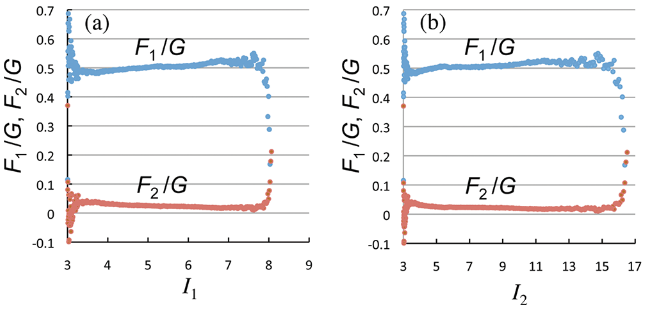

**Figure 8.** Elastic free energy derivatives as functions of (a) $I_1$ and (b) $I_2$ for PRG-5-34. Each derivative was reduced by the small strain shear modulus ($G$ = 4.9 kPa).

originates only from the volume conservation ($\lambda_x\lambda_y\lambda_z = 1$). This characteristic results in the minimal effect of the strain in one direction on the stress in the other direction under biaxial deformation. This is clearly recognizable in (1) almost no difference in $\sigma_x$ at a large $\lambda_x$ between deformations, (2) a considerably large difference between $\sigma_x$ and $\sigma_y$ in pure shear, and (3) a modest increase in $\sigma_x$ during the second stretching in the two-step biaxial deformation. The feature (1) is evident from eqs 3 and 4 at high elongation, i.e., $\sigma_x \approx G\lambda_x$ for all types of stretching, and the features (2) and (3) are also obvious from eq 3b with large $\lambda_x$ and $\lambda_y = 1$, i.e, $\sigma_y \approx G$. The stress−strain behaviors of most classical elastomers and gels disagree with these features of the neo-Hookean model,[15,18,26,27] which is shown in Figure 6. The stress−strain behavior of the PR gel with a higher cross-link concentration (PRG-10-34) exhibited qualitatively the same tendency as the classical elastomers and gels (Figure 7), and it obviously deviated from the prediction of eq 1. For PRG-10-34, $\sigma_x$ considerably depended on the type of deformation, even at a large $\lambda_x$, and the ratio $\sigma_x/\sigma_y$ in pure shear was smaller than that of the neo-Hookean model. In addition, $\sigma_x$ significantly increased in the second stretching of the two-step biaxial deformation. These features showed that the strain in one direction significantly affected the stress in the other direction. The similar behavior is also observed for a fully swollen polyacrylamide hydrogel (Figure 6). The deviation from the model prediction indicated the presence of a finite strain-coupling between different axes in addition to that resulting from volume conservation.

Even when the form of the elastic free energy ($F$) is unknown, the derivatives of $F(I_1,I_2)$ with respect to the invariants of deformation tensor $I_i$ ($i$ = 1, 2) are directly obtained from the biaxial stress−strain data with $\lambda_x \neq \lambda_y$ using the following relations:[28]

$$\frac{\partial F}{\partial I_1} = F_1 = \frac{1}{2({\lambda_x}^2 - {\lambda_y}^2)}\left[\frac{{\lambda_x}^3\sigma_x}{{\lambda_x}^2 - (\lambda_x\lambda_y)^{-2}} - \frac{{\lambda_y}^3\sigma_y}{{\lambda_y}^2 - (\lambda_x\lambda_y)^{-2}}\right] \tag{5a}$$

$$\frac{\partial F}{\partial I_2} = F_2 = \frac{-1}{2({\lambda_x}^2 - {\lambda_y}^2)}\left[\frac{\lambda_x\sigma_x}{{\lambda_x}^2 - (\lambda_x\lambda_y)^{-2}} - \frac{\lambda_y\sigma_y}{{\lambda_x}^2 - (\lambda_x\lambda_y)^{-2}}\right] \tag{5b}$$

where $I_2$ is the second strain invariant defined by $I_2 = {\lambda_x}^2{\lambda_y}^2 + {\lambda_x}^2{\lambda_z}^2 + {\lambda_z}^2{\lambda_x}^2 = {\lambda_x}^2{\lambda_y}^2 + {\lambda_x}^{-2} + {\lambda_y}^{-2}$ for incompressible materials ($\lambda_x\lambda_y\lambda_z = 1$). Figure 8 shows the dependence of the

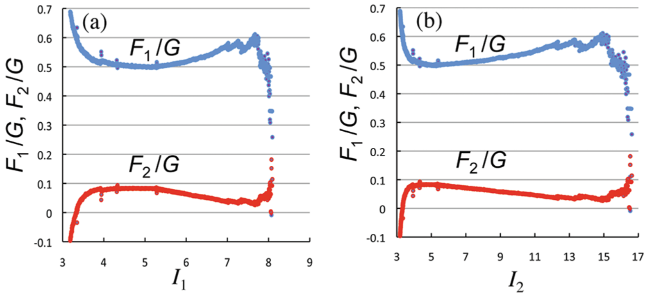

**Figure 9.** Elastic free energy derivatives as functions of (a) $I_1$ and (b) $I_2$ for PRG-10-34. Each derivative was reduced by the small strain shear modulus ($G$ = 6.4 kPa).

derivatives on each invariant for PRG-5-34 obtained from the biaxial data in Figure 5b. In the figures, each of the derivatives is reduced by the small-strain shear modulus $G$ (= 4.9 kPa).[29] The reduced derivative, $F_1/G$, is approximated to be 1/2, independently of both $I_1$ and $I_2$. Furthermore, the contribution of $F_2$ is negligibly small ($F_2/F_1 < 0.05$) in the entire strain range examined. These results (i.e., $F_1 \approx G/2$ and $F_2 \approx 0$) also confirm that $F$ is approximated by eq 1. The derivatives exhibit a pronounced upswing or downswing in the vicinities of the two limiting cases, i.e., the undeformed state ($I_1 = I_2 = 3$) and equibiaxially stretched state (i.e., $I_1 \approx 8$ and $I_2 \approx 17$), where each derivative is undefined by eq 5 because $\lambda_x = \lambda_y$. A similar behavior at small deformations has been observed in several elastomers,[26,27,30,31] but it should be noted that a small amount of error in the raw stress−strain data causes magnified errors in the calculated derivatives in the vicinities of these conditions because both the numerator and denominator in eq 5 are very small.

In contrast, PRG-10-34 exhibited a complicated dependence of the derivatives on $I_i$ ($i$ = 1, 2), as shown in Figure 9. The contribution of $F_2$ is finite, and each derivative is dependent on both $I_1$ and $I_2$. As $I_i$ ($i$ = 1, 2) increases, $F_1$ increases and $F_2$ decreases, excepting the regions near the two limiting conditions. This result indicates that the $F$ of PRG-10-34 has a far more complicated form than eq 1. We found that the $F$ for PRG-10-34 required several terms of $I_1$ and $I_2$ up to the second order to describe the biaxial data:

$$F = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + C_{11}(I_1 - 3)(I_2 - 3) + C_{20}(I_1 - 3)^2 + C_{02}(I_2 - 3)^2 \qquad (6)$$

where $C_{ij}$ ($i, j$ = 0, 1, 2) is the numerical coefficient of each term. The comparison of the data of PRG-10-34 with the prediction of eq 6 is shown together with the values of $C_{ij}$ in the Supporting Information. The validity of the same form of $F$ as eq 6 was reported in some conventional elastomers.[26,27] It should be noted that eq 6 explicitly involves the strain-coupling terms as $\lambda_i\lambda_j$ ($i, j = x, y, z$ and $i \neq j$).

A minimal strain-coupling in different directions in PRG-5-34 is expected to stem from the pulley effect of the movable cross-links. These movable cross-links possess a function to maximize the configurational entropy of the deformed network, in other words, a function to homogenize the network configuration in the deformed state. Such a pulley effect will lead to a considerable decoupling between the imposed biaxial strains in different directions. As a result, the influence of the strain in one direction on the stress in the other direction becomes minimal, and it only originates from the condition of volume conservation. The neo-Hookean model using Gaussian chain statistics leads to unrealistic results for network extensibility, i.e., infinite extensibility.[13,32] The appreciable strain hardening observed at large deformation can be attributed to the finite extensibility of the network strands of PR. It should also be noted that many free CD molecules (not incorporated into cross-linkage) are expected to move to the ends of the PR chains together with the cross-linked CDs under high stretching. This localization of the CD molecules may lower the extensibility of the PR chains.

In contrast, PRG-10-34 exhibited qualitatively the same features in the nonlinear stress−strain behavior as classical elastomers and gels. This result shows that the appearance of the neo-Hookean-like behavior in PR gels requires a sufficiently low cross-link concentration. High cross-link concentrations substantially suppressed the mobility of individual slide-rings along the network strands. As a result, the PR gels with high concentrations exhibited stress−strain behaviors similar to the classical elastomers and gels with topologically fixed cross-links.

Although PRG-5-34 exhibits a neo-Hookean-like stress−strain behavior, the molecular interpretation of the magnitude of $G$ remains to be understood. The ideal rubber elasticity model correlates $G$ with the number density of elastically effective network strands ($\nu$) as $G = \nu kT$, where $k$ and $T$ are the Boltzmann constant and temperature, respectively. If we employ this relation for PRG-5-34, the number of cross-links (pairs of intermolecular linked $\alpha$-CDs) per single PR chain ($N_c$) is estimated to be two or three. Even if we consider the full thermal fluctuation of cross-links in the framework of classical model (phantom network model),[13,17,32] the $N_c$ value remains the double (i.e., four or six) in the case of tetra-functional cross-links. These $N_c$ values are too small as compared to the value of $N_c$ (of the order of $10^2$) estimated for the case where all cross-linker molecules in the feed are converted into effective intermolecular cross-linkages, even if a finite amount of cross-linker is not consumed for effective cross-linking. As described before, the intramolecular cross-linkage is considerably suppressed under the cross-linking conditions in the present study. Furthermore, the difference in $N_c$ estimated from $G = \nu kT$ for PRG-5-34 ($G$ = 4.9 kPa) and PRG-10-34 ($G$ = 6.4 kPa) is too small (only unity) to explain the substantially different stress−strain behavior in these two PR gels. This unexpectedly small estimate of $N_c$ may imply that the equilibrium modulus of the PR gels does not simply obey the classical concept of rubber elasticity; i.e., the equilibrium modulus is not simply proportional to the number of intermolecular cross-linkage. The movable slide-rings are expected to be much less elastically effective to the modulus than the covalent cross-links. The theoretical description of the relation between the modulus and molecular structure in the PR gels is a challenging issue. Regarding this issue, in addition to the classical slip-link models (refs 33−35), a concept considering the configurational entropy of movable free CD molecules on the PR chains[36,37] is proposed to interpret the unexpectedly small equilibrium modulus for the PR gels. The quantitative assessment of $G$ on the basis of this concept is beyond the scope of the present paper, and it will be made in a separate work. Thus, neo-Hookean like behavior observed here indicates a minimal strain-coupling between the different axes in the PR gels, but this behavior should be considered to be phenomenological and treated with caution for the molecular interpretation.

How the pulley effect of movable cross-links causes a considerable strain-decoupling is an interesting theoretical question in soft matter physics. PR gels possess many molecular parameters such as $c_{PR}$, $c_x$, the CD filling rate, and the PR chain length.

The influences of these molecular parameters on the nonlinear elasticity and equilibrium modulus of PR gels remain to be characterized experimentally. In addition, the biaxial stress−strain data of the PR gels with varying the molecular parameters will be compared to the existing molecular model such as slip-link model.[34] Further investigation involving the systematic varying of these parameters will elucidate the origin of the peculiar rubber elasticity of PR gels as a new type of elastomer.

## SUMMARY

General biaxial strain testing revealed a peculiar feature of nonlinear elasticity of the PR gels. The effect of the strain in one direction on the stress in the other direction was minimal. The stress−strain relations under various types of deformation were exceptionally close to the predictions of the ideal classical theory of rubber elasticity (neo-Hookean model) with a minimal strain-coupling which results only from volume conservation. The minimal strain-coupling is a marked feature of the PR gels with movable cross-links having a function to vary the network topology in response to imposed deformation.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Figures showing comparison of the experimental stress−strain curves for PRG-10-34 with the ones calculated by eq 6 for pure shear, equibiaxial, uniaxial stretching (left) and for two-step biaxial deformation (right). This material is available free of charge via the Internet at http://pubs.acs.org.

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